Indian J. Phys. **50**, 849–852 (1976)

Wide line NMR investigation for some organic solids at room temperature

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(*Received* 12 *September* 1975, *revised* 16 *February* 1976)

The proton magnetic resonance studies of *o*-nitro benzoic acid, *m*-nitro benzoic acid and *p*-hydroxy benzoic acid were made to gain information regarding the rigidity of the crystal lattice and the molecular motions (if present) at room temperature

1. Introduction

The knowledge of crystal and the molecular structures, informations regarding the rigidity of the crystal lattice and the molecular motions have been and remain among the most fruitful and fascinating aspects invetigated by nuclear magnetic resonance spectroscopy

The present investigations concern with the proton magnetic resonance investigation of *o*-nitro benzoic, *m*-nitro benzoic acid and *p*-hydroxy Benzoic acid at room temperature (26°C) The studies were made to confirm their molecular structure and to reveal the rigidity of the crystal lattice and the nature of the molecular motions (if present) at room temperature

2. Crystal structure

o-nitro and m-nitro benzoic acid

In the absence of any precise data regarding the crystal structure of *o*-nitro and *m*-nitro benzoic acid we have assumed the structure approximately the same as that of *p*-nitro benzoic acid.

A preliminary structure analysis of *p*-nitro benzoic acid was reported by Sakore & Pant (1965) Later (1966) they reported a 3 dimensional refinement of the structure. The average C–C bond length in the benzene ring is 1.396Å which is not significantly different from the value 1.393Å found in crystalline benzene by Cox *et al* (1958)

p-hydroxy benzoic acid

In case of *p*-hydroxy benzoic acid the C–O bond length connecting the hydroxy gr up is taken as 1.375Å and O–H bond length 0.960Å.

3. Theory and Calculations

The theoretical rigid lattice value of second-moment was calculated from the expression based on Van-vleck's theory (1948) for polycrystalline sample. The second-moment consists of two parts, the intra molecular contribution (S_a) and inter molecular contribution (S_e). The intra molecular contribution for protons protons was given by

$$S_1 = \frac{6}{5} \frac{(I+1)^2 N^{-1}}{I} \sum_{j>k} \gamma_{jk}^{-6} \text{ gauss}^2$$

where I is the spin number, N is the number of magnetic nuclei over which the sum is taken and γ_{jk} is the inter nuclear distance between j-th and k-th nuclei. Using Bearden & Watt's (1951) values of physical constants and putting $I = \frac{1}{2}$ the above equation simplifies as

$$S_1 = \frac{715.9}{N} \sum_{j>k} \gamma_{jk}^{-6} \text{ gauss}^2$$

The intramolecular contribution to the second-moment thus can be calculated for any given molecular structure and are estimated to be 5.58 gauss^2 and 5.87 gauss^2 for o-nitro and m-nitro benzoic acids and 5.03 gauss^2 for p-hydroxy benzoic acid.

An accurate evaluation of the intermolecular contribution to the second-moment necessitates a knowledge of the dispositions of the molecules in the lattice. Therefore the calculation of intermolecular contribution were made applying the method adopted by Andrew & Eades (1953) and were estimated approximately to be about 6.7 gauss^2 for substituted benzoic acids as determined by Saxena & Gupta (1972). The total rigid lattice second-moments were thus estimated to be about 12.28 gauss^2, 12.57 gauss^2 for the ortho and meta nitro benzoic acids and 11.73 gauss^2 for p-hydroxy benzoic acid.

4. Experimental Details and Accuracy of Results

The experiment was performed using a Varian Associates variable frequency broad line NMR spectrometer and 12″ magnet system. The records were taken at 7.5 Mc/Sec. at Tata Institute of Fundamental Research, Bombay. The accuracy in the measurements of experimental second moments from derivative traces was approximately ± 1.0 gauss^2.

5. Experimental Results

The experimental values of second-moments at 25°C were calculated from the recorded tracings of the line shape derivatives $g'(H)$ by means of the expression

where H_0 is the resonance field value and hm is the amplitude of the sinusoidal field modulation, Andrew (1953). The above expression may be reduced to a

$$S = \frac{1}{3} \frac{\int_0^\infty g'(H)(H-H_0)^3 dH}{\int_0^\infty g'(H)(H-H_0)dH} - 1/4hm^2$$

simpler form by applying the trapezium rule Pake *et al* (1948) to the above integrals The simplified expression thus obtained is

$$S = \frac{\Sigma h^3 f(h)}{3\Sigma h f(h)} - 1/4hm^2$$

The experimental second-moment is found to be 10 51 gauss^2 and 11.25 gauss^2 for *o*-nitro and *m*-nitro benzoic acids respectively and 11 56 gauss^2 for *p*-hydroxy benzoic acid at room temperature

6. Discussions

The theoretical rigid lattice value of the second-moment for substituted benzoic acids are quite consistent with the experimentally observed values at 25°C This indicates that lattice of these compounds are rigid at lower temperatures no molecular motion exists at room temperature

The experimental results indicate that the second-moment for *o*-nitro benzoic acid is less than that of *m*-nitro benzoic acid. This discripancy in the result may be due to the ortho effect because Smyth (1927) and Smallwood (1950) have observed that the dipole moments for ortho compounds were some what lower than that of its expected value

Dielectric relaxation times of ortho, meta and para nitro benzoid acids have been determined at 3 cm microwave region t 30°C by Ahmed &Saxena (1966) The relaxation times of the compounds are found to decrease in the order, ortho, meta and para though the size of the molecules are approximately same Ahmed & Saxena (1966) in their re-orientation of COOH about its *C*-axis and at the same time stated that interactions between nitro and COOH groups producing hindrance to the rotation of COOH group In case of ortho and meta nitro benzoic acids hindrance to the rotation of COOH group is large confieming that lattice is rigid at room temperature thus confirming our present investigations.

Due to certain experimental difficulties it was not possible for us to perform experimental work over a wide range of temperature but there is possibility of re-orientation of Carboxyl group about the C–C bond with rise of temperature,

The molecular motion in these substituted benzoic acids may also exist as in the case of benzene (Andres 1950) at higher temperature.

Acknowledgment

The authors are highly indevted to Prof. B. C Gokhale for his interest and continuous encouragement through out the work Thanks are also due to Prof. R Vijayaraghavan for his generous help and providing experimental facilities at T.I F R , Bombay.

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